



Preparation and characterization of Ag-doped crystalline titania for photocatalysis applications

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ABSTRACT

Five pure and silver-enriched TiO₂ catalysts with various Ag loading (0–5.2 wt.%) were prepared by the sol–gel technique from nonionic surfactant Triton X-114, cyclohexane, water (or water solution of AgNO₃) and metal precursor. Calcination at 400 °C for 4 h was applied to convert prepared gels to pure anatase crystalline powders. Effects of silver doping on titanium photocatalyst properties were evaluated by nitrogen physical adsorption, X-ray diffraction, elemental analysis, transmission electron microscopy, Raman spectroscopy, TGA analysis and UV–vis spectroscopy.

Two “green” photocatalytic reactions were chosen for photocatalytic experiments: photocatalytic reduction of CO₂ and photocatalytic oxidation of 4-chlorophenol (4-CP) water solution. Both photocatalytic reactions were carried at mild conditions (room temperature and ambient pressure or pH 7). The activity of titania catalysts for photocatalytic reduction of CO₂ was evaluated individually with respect to various UV lamps (254 and 365 nm). The UV lamp with wavelength in the range 250–420 with highest maxima at 254 and 365 nm was used for photocatalytic oxidation of 4-CP. The dependence of the photocatalytic activity on increase of Ag content was evaluated for both reactions and compared with the photocatalytic activity of Degussa catalyst P25.

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1. Introduction

Nowadays, photocatalysis has been applied as a promising technique for decontamination, purification and/or deodorization of air as well as wastewaters [1–4]. Titania (TiO₂) has been considered to be the most suitable catalyst for these environmental applications owing to its nontoxicity, biological and chemical inertnesses, strong oxidizing power and the long-term stability against corrosion [5–10]. Therefore, a great effort has been spent on revealing and improving its photocatalytic activity for practical applications [11–13].

It is well known that the photocatalytic activity of titania depends on its crystalline structure, doping, surface area, surface hydroxyl group, etc. Recently, much scientific attention has been attracted by the effect of doping [14–17]. Silver among the other metals thanks to its high stability and excellent electrical and thermal conductivity seems to be an auspicious titania dopant. For those reasons a doping effect of silver on the titania photocatalytic efficiency in decontamination processes has been intensively studied

[18,19]. Moreover, also the silver ability to prevent the backward recombination of a promoted electron (e[−]) and a generated hole (h⁺) can positively effect the photocatalytic activity of titania.

To verify the doping effect of silver the present study is focused on preparation, thorough characterization and application of the prepared titania catalysts in the wide range of silver doping.

Two reactions were chosen for photocatalytic experiments: photocatalytic reduction of carbon dioxide and photocatalytic oxidation of 4-chlorophenol (4-CP). Carbon dioxide (CO₂) belongs to the most important greenhouse gases, therefore, the reduction of CO₂ is an issue drawing the attention of many researchers. The reduction of CO₂ over photocatalysts is one of the most promising methods since CO₂ can be reduced to useful compounds by irradiating with UV light at room temperature and ambient pressure.

Photocatalytic oxidation of 4-CP was chosen owing to that 4-CP is frequently used for production of dyes, fungicides and drugs [20] and it belongs between toxic and non-biodegradable organic compounds. Its removal from wastewaters is currently performed by conventional treatment methods usually under environmentally unfriendly conditions (e.g. low pH, high temperature). Thus photocatalytic oxidation of 4-CP over suitable catalysts has been accepted as a promising alternative. This reaction does not utilize any additional chemicals and can be applied at room temperature

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[21]; nevertheless, for the reaction acceleration a low pH about 3 has been usually used [22,23]. Therefore, the evaluation of the silver doping effect on photocatalytic oxidation of 4-CP has been studied at environmentally friendly conditions in this work.

2. Experimental

2.1. Sample preparation

Pure and silver-enriched TiO_2 powders were prepared by the sol–gel process controlled in a reverse micellar environment. Pure TiO_2 was synthesized by the addition of titanium (IV) isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, Aldrich, >97%) into formed inverse micellar solution made of cyclohexane (Aldrich, 99.9+%, HPLC grade), nonionic surfactant Triton X-114 ($\text{C}_{27}\text{H}_{48}\text{O}_{7.5}$, Aldrich) and distilled water. The molar ratio of cyclohexane/Triton X-114/water/ $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was kept at 11/1/1/1 (volume ratio TX-114/cyclohexane = 0.49) [24]. The beaker with the solution made of appropriate amount of cyclohexane, Triton X and water was being stirred intensively for 15 min for homogenization and formation of inverse micelles. Then liquid titanium (IV) isopropoxide was regularly dropped to the micellar solution during the vigorous stirring. The drop by drop addition of isopropoxide into the sol changed the state from transparent to viscous yellow. After the addition of all amount of isopropoxide the sol was being stirred for another 10 min. For the preparation of powders the sol was left in a bowl on air for 24 h. The obtained rigid gel was calcined at 400 °C for 4 h with the temperature ramp 1 °C/min in the air flow in a muffle furnace.

Variously, Ag-enriched TiO_2 samples were prepared analogically: AgNO_3 (Aldrich, 99.9999%) solution of appropriate concentration (0.25 M, 0.75 M, 1.3 M and 1.85 M) was added instead of distilled water during catalyst preparation.

2.2. Characterization

Textural properties of samples (S_{BET} , S_{meso} , V_{micro} , pore-size distribution) were evaluated from the nitrogen physical adsorption–desorption isotherms at 77 K obtained with the ASAP2020M instrument (Micromeritics, USA). Before analysis samples were dried at 105 °C at least for 12 h *in vacuo* (1 Pa). The mesopore surface area (S_{meso}) and the micropore volume (V_{micro}) were evaluated from the measured nitrogen physical adsorption–desorption isotherms by two independent methods; modified BET equation [25] and *t*-plot constructed with the use of Leclux–Pirard standard isotherm [26]. Results obtained by both methods were identical without discrepancies. Pore-size (r_p) was determined by the advanced BJH method.

X-ray diffraction (XRD) patterns were measured with the PANalytical X'Pert MPD diffractometer and the Cu $K\alpha$ radiation. Measurements were done in the Bragg–Brentano geometry with the variable slits and the linear detector. The wide range of diffraction angles $2\theta = 8\text{--}140^\circ$ was scanned. In order to correct diffraction line broadening effects for the instrumental broadening the NIST LaB_6 profile standard was measured in the same experimental setups. The diameter of crystallites was evaluated by the Rietveld-like fitting of the whole diffraction patterns using the MStruct program [27,28].

For determination of crystallinity and purity (the origin of possible carbon contamination) of pure and Ag-enriched titania Raman spectroscopy was performed on dispersive Raman spectrometer Nicolet Almega XR connected with confocal microscope Olympus BX51. Raman spectra were measured using the blue line 473 nm from the semiconductor laser. Samples were deposited on the wolfram substrate and scanned using the lens with 10 \times magnification

at 16% of energy (to suppress possible influence of the original crystallinity of samples). The width of slit was 100 μm .

Fractions of prepared granulated samples in the range 0.25–0.50 mm were used for measurement of the UV–vis diffuse reflectance spectra recorded by GBS CINTRA 303 spectrometer equipped with a diffuse reflectance attachment with a spectralon-coated integrating sphere against a spectralon reference. The reflectances were re-calculated to the absorption using the Schuster–Kubelka–Munk equation, $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. All catalysts were also measured in dehydrated form at 400 °C in oxygen.

Ag-to- TiO_2 mass ratio in Ag/ TiO_2 samples were determined by XRF analysis using an ARL 9400 XP sequential WD-XRF spectrometer with the standard deviation lower than 5%.

TGA analysis of raw gels was performed on a Santon-Redcroft TG-750 thermobalance with temperature ramp 1 °C/min on air.

Transmission electron micrographs were determined on unstained ultrathin sections using the Philips CM100 electron microscope at 80 kV and appropriate magnification. Digital images were recorded with a MegaViewII slow scan camera and processed with the AnalySis 3.2 software.

The purity (carbon content in weight %) of samples was specified on an Elementar Vario EL III (Elementar). TiO_2 powder (approximately 5 mg) was burnt in oxygen atmosphere at high temperature (up to 1200 °C). Gaseous products (N_2 , CO_2 , H_2O and SO_2) were purified, separated to individual components and analyzed on TCD detector. Each sample was analyzed thrice to confirm the reliability of results. The detection limit of the apparatus was 0.1 wt.%.

2.3. Photocatalytic experiments

Two reactions were chosen for photocatalytic experiments. The first one was the photocatalytic reduction of carbon dioxide by water [29] that was carried out in a stirred batch annular reactor with a suspended catalyst illuminated by UV 8 W Hg lamps (254 and 365 nm).

Typical intensities of Pen-Ray Lamps (microwatts/cm²) according to producers:

Model 11SC-1	(254 nm)	4750 microwatts/cm ²
Model 11SC-1	(365 nm)	1255 microwatts/cm ²

Catalyst powder (0.1 g) was suspended in 100 ml of 0.2 M NaOH solutions, supercritical-fluid-grade CO_2 with a certified maximum of hydrocarbons less than 1 ppm was used as the reactant (SIAD Technical Gases, CZ). GC/FID/TCD was used for the analysis of gas and liquid reaction products. During kinetic measurements the influence of transport phenomena was minimized. The elimination of CO_2 diffusion from the bulk of gas through the gas–liquid interface in a laboratory batch slurry reactor was accomplished by saturating the liquid with pure CO_2 before the reaction had been started [30,31]. Catalyst loading of 1 g dm^{−3} was chosen to avoid concentration gradients in the bulk of stirred liquid with TiO_2 suspension due to the scattering effect of light caused by the high TiO_2 concentration [31–34]. The determination of the suitable volume (100 ml) of the liquid phase in our annular photoreactor to fulfil the requirement of perfect mixing has been published recently [35]. The experimental errors for all samples were determined from repeated experiments and they varied between 5 and 10%.

As the second reaction the photocatalytic oxidation of 4-CP water solution (concentration 500 mg/l) was used. It was provided in the batch system with TiO_2 or Ag doped TiO_2 photocatalysts. Approximately 0.025 g of catalysts was applied to 200 ml of the 4-CP solution at the pH 7 in the presence of UV light. For the photocatalysis the UV lamp Philips HOK 4/120 SE, 400 W medium pressure mercury lamp with wavelength in the range 250–420 nm was applied. The Erlenmeyer flasks with the 4-CP solution and

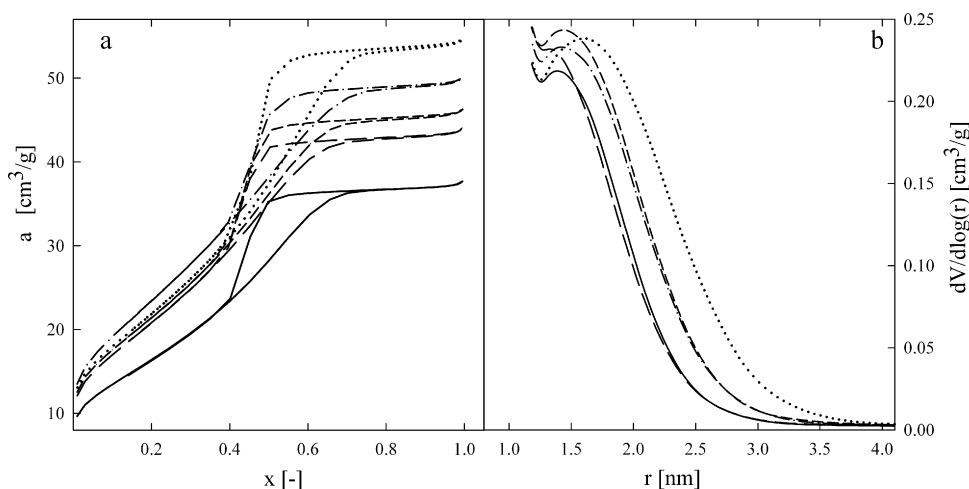


Fig. 1. (a) Nitrogen adsorption–desorption isotherms; (b) pore-size distributions evaluated from desorption branches of nitrogen isotherms; (—) TiO_2 , (---) 0.7AgTiO_2 , (- · -) 2.4AgTiO_2 , (— · —) 3.4AgTiO_2 , (.....) 5.2AgTiO_2 .

the catalyst carrier were placed on the orbital shaker (320 rpm) at the laboratory temperature below the UV light source. Concentrations of the 4-CP in the solution were analyzed by HPLC (BIO TEC Instruments, Diode Array Detector Column Merck Lichnosorb) with 60 min sampling interval.

3. Results and discussion

3.1. Catalyst characterization

Five titania photocatalysts with various amounts of Ag were prepared for activity testing in “green” photocatalytic reactions. The relatively wide range of Ag content (0.7–5.2 wt.%) guaranteed better evaluation of Ag presence on photocatalytic efficiency as well on changes in catalyst properties. Purity of all synthesized photocatalysts was excellent. The repeatedly ($3\times$) measured carbon content for the each sample was undetectable (below 0.1 wt.%; detection limit). This affirms the appropriateness of the selected calcination temperature (400 °C), which was also confirmed by TGA analysis.

Structural and textural properties (BET surface area, S_{BET} , mesopore surface area, S_{meso} , micropore volume, V_{micro} , and maximum of pore-radius, r_{max}) together with silver content of synthesized photocatalysts and the reference industrial catalyst Degussa P25 are summarized in Table 1. The content of silver in all synthesized

samples was measured repeatedly for independently prepared samples with maximum deviation less than 1%.

In Fig. 1a nitrogen adsorption–desorption isotherms (at 77 K, a – adsorbate volume per gram of adsorbent) are shown for all samples. Nitrogen isotherms for titania as well as Ag doped titania samples are very similar and reveal combination of I and IV isotherm types (IUPAC classification). For all samples high adsorption at low x can be seen, which confirms the presence of micropores. A steep part of hysteresis loop ($x = p/p_0$ between 0.4 and 0.5) points to relatively narrow pore-size distribution.

Mesopore surface areas of synthesized photocatalysts are relatively high (50–58 m^2/g) and all catalysts include micropores. It is evident that even a small addition of Ag (0.7%) increases the mesopore surface area (about 20%) and the micropore volume (about 10%). The additional increase of Ag content up to 5.2% had nearly no effect on values of the surface area but it increases the micropores volume about 30% in comparison with the pure titania sample.

BET surface areas for all samples varied between 67 and 80 m^2/g and are presented only for comparison with literature. However, these values are incorrect owing to the presence of micropores in all samples; BET isotherm equation can be used only for materials without micropores [36].

In Fig. 1b the pore-size distributions evaluated from desorption branches of nitrogen isotherms are presented. The slight increase of pore-sizes (with r_{max} shifted from 1.4 to 1.6 nm) with increasing Ag

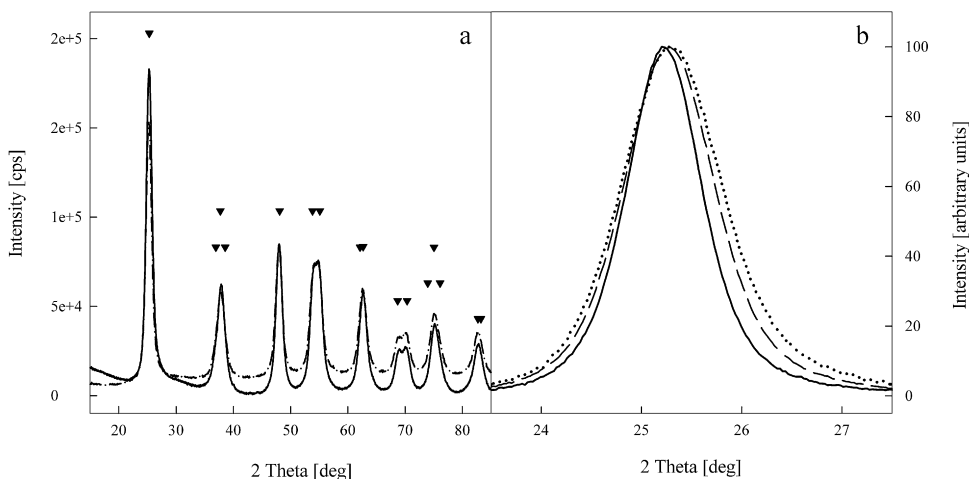


Fig. 2. (a) Diffraction lines; (—) TiO_2 , (---) 0.7AgTiO_2 , (▼) anatase; (b) fitted distribution curves of crystallite sizes; (—) TiO_2 , (---) 0.7AgTiO_2 , (.....) 5.2AgTiO_2 .

like species. However, it is difficult to identify the individual Ag species supported on TiO_2 owing to the intensive UV–vis bands of TiO_2 that overlap the UV–vis bands corresponding to Ag species. Pure TiO_2 exhibits broad absorption band below 400 nm (above $25,000\text{ cm}^{-1}$) due to a charge-transfer transition between the lattice oxygen ligands and a central titanium ion. Ag^+ ions supported on inorganic supports are characteristic by the UV–vis bands at $\sim 240\text{ nm}$ ($41,600\text{ cm}^{-1}$) and $\sim 210\text{ nm}$ ($47,600\text{ cm}^{-1}$) [38–41]. Small Ag clusters have been reported to be detected by the UV–vis bands with a maximum between 250 and 330 nm ($30,000\text{--}40,000\text{ cm}^{-1}$) [38,40]. Large Ag clusters might be detected by the UV–vis bands with a maximum at 400–500 nm ($25,000\text{--}20,000\text{ cm}^{-1}$) [40,41].

The UV–vis spectra of AgTiO_2 catalysts (Fig. 5a) exhibited an intensive band with a maximum at 360 nm that might be ascribed to pure TiO_2 support. The UV–vis spectra of 2.4 AgTiO_2 , 3.4 AgTiO_2 and 5.2 AgTiO_2 catalysts contained the intensive shoulder at 500–900 nm that might be attributed to the presence of Ag clusters [42] or to the surface plasmon absorption of spatially confined electrons in Ag nanoparticles [15,43,44]. On the other hand, this UV–vis band was not observed in the UV–vis spectra of 0.7 AgTiO_2 catalyst. Thus, the preparation of Ag doped TiO_2 catalyst with a low Ag concentration led to the material without the presence of metallic Ag clusters; these species clearly formed around 2 wt.% Ag. The energy edge decreased with the increasing Ag content (detail Fig. 5a).

Fig. 5b shows the UV–vis spectra of dehydrated materials. The presence of the small metallic Ag clusters and silver-oxide like species might be excluded from the Ag doped TiO_2 catalysts, as the UV–vis band above 400 nm was not observed at the UV–vis spectra of dehydrated Ag– TiO_2 materials (Fig. 5b). This indicates that the small metallic Ag clusters are easily transformed to Ag^+ ions or Ag clusters under oxidizing conditions [40]. The procedure of dehydration was accompanied by the change of color from dark to yellow supporting the presence of metallic Ag species in the catalysts. The procedure of dehydration and hydration was reversible as it was evidenced by the UV–vis spectra (not shown in figures). The intensive shoulder above 450 nm appeared in the UV–vis spectra of re-hydrated AgTiO_2 catalysts above 2.4% Ag after 1 day on air. While the small metallic Ag clusters were re-establish on AgTiO_2 with 2.4 and 3.4% Ag after 1 day, the species were only partly re-established on AgTiO_2 with 5.2% Ag.

Compared to pure TiO_2 catalyst, the maximum of the UV–vis band was at around 400 nm (λ_{400}) and the absorption spectrum was shifted for Ag doped TiO_2 catalysts into the visible region. Thus the increasing Ag content on TiO_2 support increased the visible absorbance capacity of the photocatalysts. Moreover, for both types of catalysts the energy edge (E_g) decreased with increasing amount of silver as it is shown at details of Fig. 5a and b. Nevertheless, the presence of the intensive shoulder at 500–900 nm for 2.4 AgTiO_2 , 3.4 AgTiO_2 and 5.2 AgTiO_2 catalysts (see Fig. 5a) significantly influences the dependence of the energy edge on the silver content for prepared catalysts, thus linear function was evaluated only for dehydrated catalysts. The increase of the maximum absorption wavelength was approximately linear up to 3.4 wt.% Ag owing to that 5.2 AgTiO_2 catalysts exhibited the similar maximum absorption wavelength as 3.4 AgTiO_2 catalyst (see Fig. 5b). The decrease in the energy edge on Ag– TiO_2 materials compared to the TiO_2 support was attributed to the electron acceptor character of the surface silver nanoparticles [44].

3.2. Photocatalytic reactions

3.2.1. Photocatalytic reduction of CO_2

The effect of Ag loading on the photocatalytic reduction activity of prepared titania photocatalysts was studied under two lamps with maximum irradiation at 254 and 365 nm over a period of

0–24 h. As reaction products plenty of chemical compounds such as hydrogen, carbon monoxide, methane, methanol, formic acid, formaldehyde, ethane and ethylene could be formed [30,45]; nevertheless, only two products, methane in gas phase and methanol in liquid phase were determined as the main products. Therefore, the sum of these products during 24 h was used for comparison of the photocatalytic activity. For the purpose of comparing, the data from the longest reaction time span were chosen owing to that yields were the highest and therefore the most accurate (more details see in our previous publication [29]).

The sums of methanol and methane yields of all prepared and commercial Degussa catalysts are for both lamps compared in Fig. 6. For lamp 254 nm all Ag doped TiO_2 photocatalysts revealed significantly higher photoactivity than pure TiO_2 . The increase of the main product yields with the growth of Ag loading was detected (disproportion between 0.7 and 2.4 AgTiO_2 catalysts is caused by experimental error). The main product yield for Degussa catalyst was the lowest, which could correlate with its lower specific surface area. In this sense, doping with Ag could make a triple effect: (i) even the small addition of Ag (0.7 wt.%) increases the specific surface areas of TiO_2 significantly. It makes that the Ag doped sol–gel TiO_2 catalysts possess the higher photocatalytic activity. (ii) Ag doping could reduce the band gap energy, which promotes the photocatalytic activity, too. (iii) Ag could provoke a decrease in electron–hole recombination rate, acting as electron traps [46,47]. This hypothesis was based on the fact that the electron transfer from TiO_2 conduction band to silver particles at the interface is thermodynamically possible because the Fermi level of TiO_2 is higher than that of silver metals. Such phenomenon would be expected to lead to the formation of Schottky barrier at metal–semiconductor contact region, which could improve the charge separation and consequently the photocatalytic activity of TiO_2 .

The sum of methanol and methane yields for all catalysts under 365 nm lamp was significantly lower than for 254 nm lamp, which corresponds with its lower energy. The difference between intensities of lamps could also participate on the smaller yields of products at 365 nm. The differences of yields between individual catalysts were negligible, nonetheless, the Degussa catalyst revealed the lowest activity of all. Despite the expected increasing yields with the increase of Ag-content, it was not noticeable due to experimental error.

3.2.2. Photocatalytic oxidation of 4-CP water solution

To evaluate the influence of the silver loading on the photocatalytic oxidation activity of titania catalysts the photodegradation of 4-CP was studied at room temperature and pH 7. The initial concentration of 4-CP was relatively high – 4 mM and the amount of catalyst relatively low 0.125 g/l compared to literature [2,3,48,49].

The obtained results are summarized in Fig. 7, where time dependences of 4-CP degradation are compared for Degussa and four prepared catalysts except of 0.7 AgTiO_2 catalyst. Time dependence of 4-CP degradation of 0.7 AgTiO_2 copied pure TiO_2 catalyst, thus, both curves are identical. During the first two hours the quick decrease of 4-CP relative concentration can be easily recorded. The concentration of 4-CP fell down to 52–60% of initial concentration for all tested catalysts except of 2.4 AgTiO_2 catalyst for which the 4-CP concentration decreased to less than 40% of the initial concentration. After seven hours differences of the 4-CP remain fractions for all catalysts were relatively small, only about eight percents; between 15% for 2.4 AgTiO_2 catalyst to 23% for pure TiO_2 . Nevertheless, after 20 h the remain fractions of 4-CP got down to nearly zero (maximum 1.6% for pure titania catalyst) for all tested catalyst except of Degussa catalyst, which photocatalytic activity was distinctly lower. It is noticeable that the presence of silver in titania catalysts had a positive effect on their photocatalytic activity, with 2.4% of Ag loading revealing the maximum efficiency.

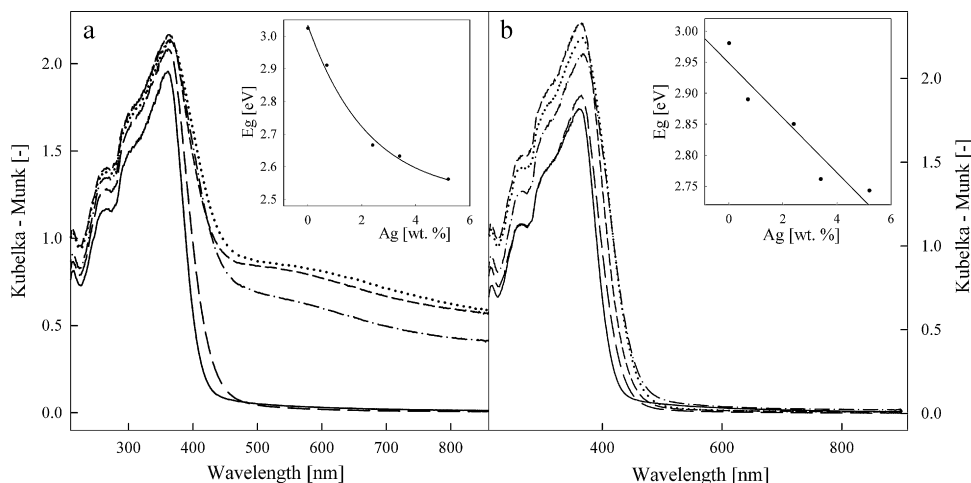


Fig. 5. (a) UV-vis spectra of AgTiO₂ catalysts, detail – the energy edge of prepared catalysts; (b) UV-vis spectra of dehydrated catalysts, detail – the energy edge of dehydrated catalysts; (—) TiO₂, (— —) 0.7AgTiO₂, (- - -) 2.4AgTiO₂, (- . -) 3.4AgTiO₂, (.....) 5.2AgTiO₂.

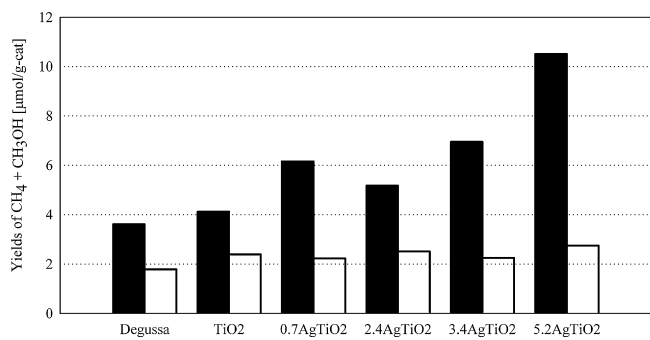


Fig. 6. Sums of methanol and methane yields of all prepared and Degussa catalysts; 254 nm lamp – dark, 365 nm lamp – light.

Reproducibility of experiments is shown in detail of Fig. 7, where results of two 4-CP degradation experiments over 5.2AgTiO₂ catalyst in logarithmic scale are shown. It is seen that reproducibility of experiments is excellent with maximal std. error 3% with linear character, which affirms data from literature: the pseudo-first order for the 4-CP photocatalytic degradation.

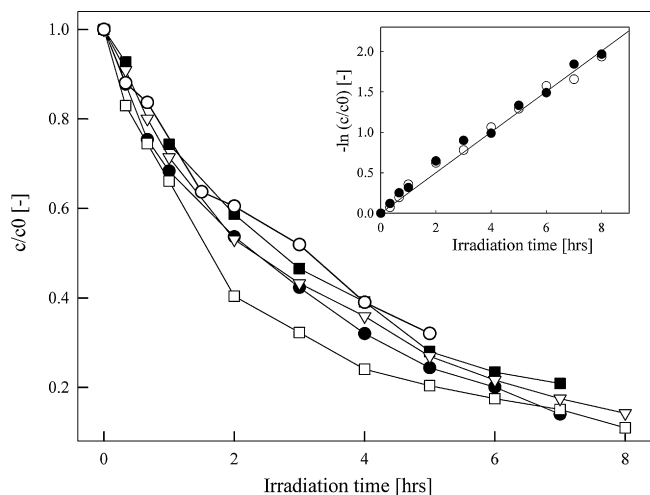


Fig. 7. Time dependences of 4-CP degradation; detail: reproducibility of experiments, results of two independent experiments over 5.2AgTiO₂ catalyst in logarithmic scale; (○) Degussa (■) TiO₂, (□) 2.4AgTiO₂, (●) 3.4AgTiO₂, (△) 5.2AgTiO₂.

4. Conclusions

Five titania photocatalysts with various silver loading (0–5.2 wt.%) were synthesized. Prepared photocatalysts possessed relatively high surface area with the low amount of micropores and an excellent purity. Anatase was detected by XRD and Raman spectroscopy as the only crystallite form in all catalysts. It was proved that silver presence suppressed the grow of titania crystals in dependence on the Ag content. Simultaneously, even the small addition of Ag (0.7%) increased the surface area about 20% with no additional increase in dependence on the Ag content. Silver is probably mostly scattered in the TiO₂ lattice except of very small Ag crystals irregularly placed on the catalyst surface. This fact is connected with the sol gel preparation method when silver as AgNO₃ was added directly into the inverse micellar solution together with titanium (IV) isopropoxide. Compared to pure TiO₂ catalyst the absorption spectra for Ag doped TiO₂ catalysts were shifted into the visible region. Thus the increasing Ag content on TiO₂ support increased the visible absorbance capacity of the photocatalysts with the approximately linear dependence up to 3.4 wt.% Ag and simultaneously decreased the energy edge of catalysts. The ability of easy reversible transformation of Ag metallic clusters to Ag⁺ ions under oxidizing conditions for catalysts with Ag content up to 3.4% was also evaluated.

The positive effect of silver doping on the photocatalytic reduction activity of titania catalysts was confirmed for the photocatalytic reduction of CO₂ but only under the lamp with wavelength at 254 nm. The increase of the main product yields (methane and methanol) in the dependence of Ag loading was clearly detected with significantly higher photoactivity of all Ag doped TiO₂ photocatalysts than pure TiO₂ or Degussa catalyst. However, this effect with the lamp of 365 wavelength was not confirmed.

The positive effect of silver doping on the titania catalyst activity was also confirmed for photocatalytic oxidation of 4-CP water solution, nevertheless, no direct dependence with the growth of Ag loading was noticed. It was verified that degradation of 4-CP over all tested catalysts can run broadly quickly also under mild conditions (room temperature, pH 7) even in the case of the relatively high initial concentration of 4-CP (4 mM) and the relatively low amount of catalyst (0.125 g/l). Thus, the tested reaction system could be promising as the environmentally friendly alternative for wastewater purification.

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